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(72) HOLDERBAUM, Martin, DE  
(72) AUMÜLLER, Alexander, DE  
(72) TRAUTH, Hubert, DE  
(72) VOIT, Guido, DE  
(72) SPERLING, Karin, DE  
(72) KRAUSE, Alfred, DE  
(71) BASF AKTIENGESELLSCHAFT, DE

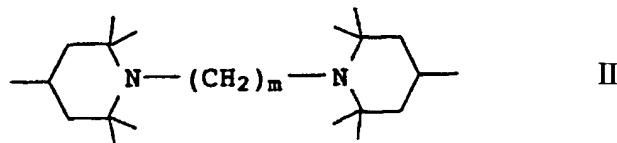
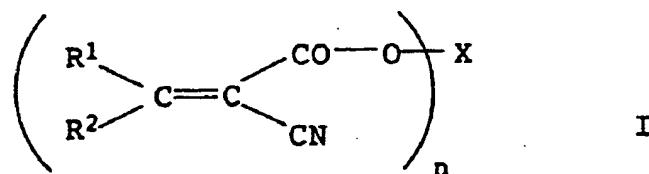
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#### (54) ESTERS D'ACIDE 2-CYANOACRYLIQUE

(54) 2-CYANOACRYLIC ACID ESTERS



(57) L'invention concerne des esters d'acide 2-cyanoacrylique (I) dans lesquels les restes ont la notation suivante: R<sup>1</sup> et R<sup>2</sup> sont hydrogène ou un reste avec une combinaison isocyclique ou hétérocyclique possédant au moins un noyau iso-aromatique ou hétéro-aromatique, l'un des restes R<sup>1</sup> ou R<sup>2</sup> devant être différent de l'hydrogène, n vaut de 2 à 10, X, lorsque n = 2, est un reste de la formule (II) où m vaut de 2 à 8, X, lorsque n > 2, est le reste d'un polyol aliphatique ou cycloaliphatique n-hydrique avec 3 à 20 atomes de C, un reste cycloaliphatique pouvant contenir également 1 à 2 hétéro-atomes, et un reste aliphatique pouvant contenir

(57) Described are 2-cyanoacrylic acid esters (I) in which the groups are defined as follows:  $R^1$  and  $R^2$  are hydrogen or a group with an isocyclic or heterocyclic ring system having at least one iso-aromatic or hetero-aromatic nucleus, whereby one of the groups  $R^1$  and  $R^2$  must be different from hydrogen,  $n$  is from 2 to 10,  $X$  in the case when  $n = 2$  is a group of the formula (II) in which  $m$  is from 2 to 8,  $X$  in the case when  $n > 2$  is an  $n$ -hydric aliphatic or cycloaliphatic polyol group with 3 to 20 C-atoms, whereby the cycloaliphatic polyol group may include 1 to 2 hetero-atoms and the aliphatic polyol group may include up to 8 non-adjacent oxygen atoms,



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dans la chaîne carbonée jusqu'à 8 atomes d'oxygène, atomes de soufre, groupes imino ou alkylimino C<sub>1</sub>-C<sub>4</sub> non adjacents. Les composés de la formule (I) s'utilisent comme filtres solaires.

sulphur atoms, imino groups or C<sub>1</sub>-C<sub>4</sub> alkylimino groups in the carbon chain. Compounds of the formula (I) are suitable for use as light-protection agents.

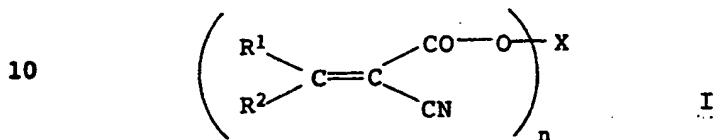


## 2-Cyanoacrylic esters

## Abstract

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## Novel 2-cyanoacrylic esters I



where the radicals have the following meanings:

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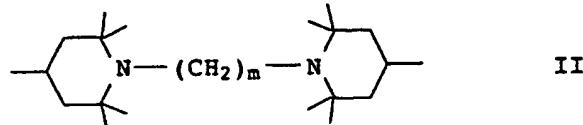
R<sup>1</sup> and R<sup>2</sup> are each hydrogen or a radical having an iso- or heterocyclic ring system with at least one iso- or heteroaromatic nucleus, and at least one of the radicals R<sup>1</sup> or R<sup>2</sup> must be different from hydrogen,

20

$n$  is from 2 to 10, and

$x$  is, when  $n = 2$ , a radical of the formula II

25



30

where  $m$  is from 2 to 8, and

X is, when n > 2, the radical of an n-hydric aliphatic or cycloaliphatic polyol having 3-20 carbon atoms, it also being possible for a cycloaliphatic radical to contain 1 or 2 hetero atoms, and for an aliphatic radical to be interrupted by up to 8 non-adjacent oxygen atoms, sulfur atoms, imino or C<sub>1</sub>-C<sub>4</sub>-alkylimino groups, are used as light stabilizers.

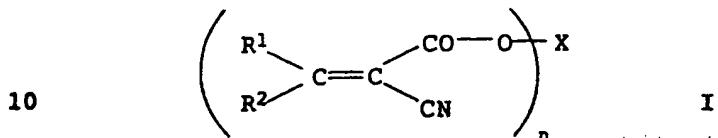
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## 2-Cyanoacrylic esters

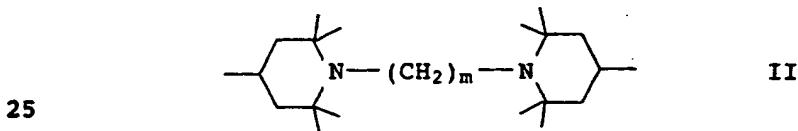
The present invention relates to novel 2-cyanoacrylic esters of  
5 the formula I



where  $R^1$  and  $R^2$  are each hydrogen or a radical having an iso- or heterocyclic ring system with at least one iso- or heteroaromatic 15 nucleus, and at least one of the radicals  $R^1$  or  $R^2$  must be different from hydrogen,

n is from 2 to 10, and

20 x is, when n = 2, a radical of the formula II



where m is from 2 to 8, and

30 x is, when n > 2, the radical of an n-hydric aliphatic or cycloaliphatic polyol having 3-20 carbon atoms, it also being possible for a cycloaliphatic radical to contain 1 or 2 hetero atoms, and for an aliphatic radical to be interrupted by up to 8 non-adjacent oxygen atoms, sulfur atoms, imino or C1-C4-alkylimino 35 groups.

The invention furthermore relates to a process for preparing the compounds I, to the use thereof as stabilizers, in particular against the action of light, for organic materials, in particular 40 for cosmetic or dermatological preparations, plastics or paints, and to organic materials which contain the compounds I.

US-A 3 215 725 and DE-A 41 22 475 disclose 2-cyanoacrylic esters of monohydric and dihydric alcohols as light stabilizers for 45 plastics and paints.

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However, these compounds have the technical disadvantage of a relatively high volatility. Since, moreover, they are only conditionally compatible with many organic materials, especially with polyolefins, they are prone, especially on storage at 5 elevated temperature, to migrate and consequently display exudation.

It is an object of the present invention to remedy these disadvantages by novel stabilizers of the 2-cyanoacrylic ester 10 type.

We have found that this object is achieved by the 2-cyanoacrylic esters of the general formula I defined at the outset.

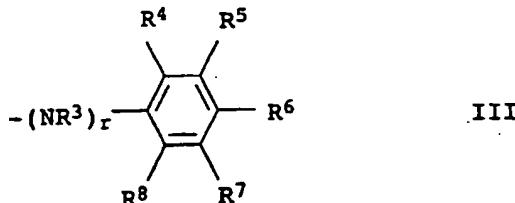
15 We have furthermore found a process for preparing these compounds, their use as light protection factors or stabilizers for organic materials, and organic formulations which contain these compounds as stabilizers.

20 If the radicals R<sup>1</sup> and R<sup>2</sup> are different, the 2-cyanoacrylic ester groups of I may be either in the cis or the trans form. The preparation of the compounds usually results in mixtures of these isomers. It is possible to separate these isomers, but this is unnecessary for most industrial applications.

25 Suitable organic radicals for R<sup>1</sup> and R<sup>2</sup> are, in general, cyclic structures which contain at least one iso- or heteroaromatic nucleus, which is preferably linked directly to the 3-C atom of the acrylic group but can also be linked to this carbon atom via 30 aliphatic or cycloaliphatic groups and via a linker -NR<sup>3</sup>-.

R<sup>1</sup> or R<sup>2</sup> is preferably a radical of the formula III

35



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where R<sup>3</sup> is hydrogen or C<sub>1</sub>-C<sub>10</sub>-alkyl, r is 0 or 1, and R<sup>4</sup> to R<sup>8</sup> are each, independently of one another, hydrogen, C<sub>1</sub>-C<sub>8</sub>-alkyl, chlorine, bromine, cyano, nitro, amino, mono(C<sub>1</sub>-C<sub>4</sub>-alkyl)amino, 45 di(C<sub>1</sub>-C<sub>4</sub>-alkyl)amino, hydroxyl, C<sub>1</sub>-C<sub>8</sub>-acyl, C<sub>1</sub>-C<sub>8</sub>-acyloxy,

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$C_1$ - $C_{18}$ -alkoxy,  $C_1$ - $C_{12}$ -alkoxycarbonyl,  $C_3$ - $C_6$ -cycloalkyl or  $C_3$ - $C_6$ -cycloalkoxycarbonyl.

Suitable radicals  $R^3$  besides hydrogen are  $C_1$ - $C_{10}$ -alkyl radicals such as methyl, ethyl, n-propyl, isopropyl, isopropyl [sic], n-propyl [sic], n-butyl, isobutyl, sec-butyl, tert-butyl, n-pentyl, isopentyl, sec-pentyl, tert-pentyl, neopentyl, n-hexyl, n-heptyl, n-octyl, isoctyl, 2-ethylhexyl, n-nonyl, isononyl, n-decyl and isodecyl.

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If one or more of the radicals  $R^4$  to  $R^8$  are  $C_1$ - $C_8$ -alkyl,  $C_1$ - $C_8$ -acyl,  $C_1$ - $C_{18}$ -alkoxy or  $C_1$ - $C_{12}$ -alkoxycarbonyl, the alkyl radicals therein can be, for example, methyl, ethyl, n-propyl, isopropyl, n-propyl [sic], n-butyl, isobutyl, sec-butyl, tert-butyl, n-pentyl, isopentyl, sec-pentyl, tert-pentyl, neopentyl, n-hexyl, n-heptyl, n-octyl or 2-ethylhexyl.

Examples of suitable longer-chain alkyl radicals in  $C_1$ - $C_{18}$ -alkoxy and  $C_1$ - $C_{12}$ -alkoxycarbonyl groups are nonyl, 2-methylnonyl, iso-20 nonyl, 2-methyloctyl, decyl, isodecyl, 2-methylnonyl [sic], undecyl, isoundecyl, dodecyl, isododecyl, tridecyl, isotridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl and octadecyl. (The terms isoctyl, isononyl, isodecyl and isotridecyl are trivial names derived from the carbonyl compounds obtained by the oxo 25 synthesis; compare in this connection Ullmann's Encyclopedia of Industrial Chemistry, 5th edition, Vol. A1, pages 290-293, and Vol. A10, pages 284 and 285).

Examples of suitable  $C_3$ - $C_6$ -cycloalkyl radicals are cyclopropyl, 30 cyclobutyl, cyclopentyl, methylcyclopentyl or cyclohexyl. These cycloalkyl groups are also suitable radicals in  $C_3$ - $C_6$ -cycloalkyl-carbonyl groups.

Preferred 2-cyanoacrylic esters I are those where  $R^3$  is hydrogen, 35 methyl or ethyl.

Further preferred 2-cyanoacrylic esters I are those where up to three, particularly preferably one, of the radicals  $R^4$  to  $R^8$  are hydrogen,  $C_1$ - $C_4$ -alkyl, chlorine, cyano, hydroxyl, acetyl, 40  $C_1$ - $C_5$ -alkoxy,  $C_1$ - $C_8$ -alkoxycarbonyl or cyclohexoxycarbonyl, and the remainder of these radicals are hydrogen.

Particularly preferred 2-cyanoacrylic esters I are those where  $R^6$  is hydroxyl, methoxy, ethoxy, propoxy, isopropoxy, butoxy, iso-45 butoxy, sec-butoxy or tert-butoxy, because such 4-substituted phenyl groups contribute to the stabilizing effect of the compounds. For the same reason, 2-cyanoacrylic esters where  $R^5$  and/or

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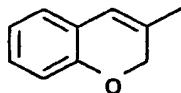
R<sup>7</sup> are hydrogen, methyl or tert-butyl, in particular when R<sup>6</sup> is hydroxyl, are also particularly preferred.

Preferred compounds I according to the invention are those where 5 r is 0.

Further preferred compounds according to the invention are those where R<sup>1</sup> or R<sup>2</sup> is hydrogen, those where R<sup>1</sup> and R<sup>2</sup> are identical radicals, and those where one of the radicals R<sup>1</sup> or R<sup>2</sup> is phenyl-10 amino, p-tolylamino, p-methoxy- or p-ethoxycarbonylphenylamino and the other is hydrogen.

Another preferred radical for R<sup>1</sup> or R<sup>2</sup> is the chroman residue Ib

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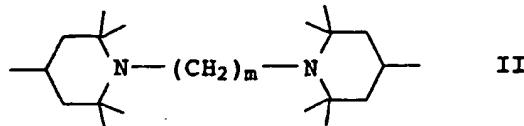
Ib

20 or its substituted derivates, because these also enhance the stabilizing effect of the compounds I.

Further suitable radicals R<sup>1</sup> and R<sup>2</sup> are heterocyclic groups such as substituted or unsubstituted thiophenyl [sic], furfuryl and 25 pyridyl radicals.

If n = 2, X is a radical of the formula II

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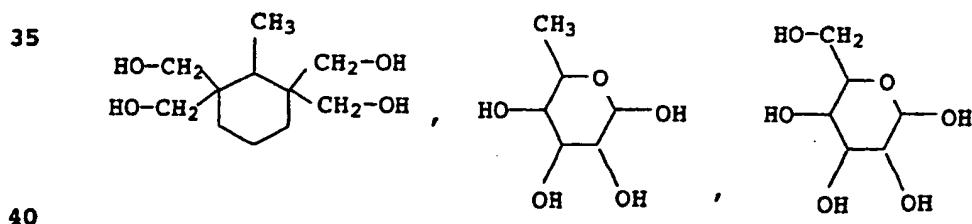
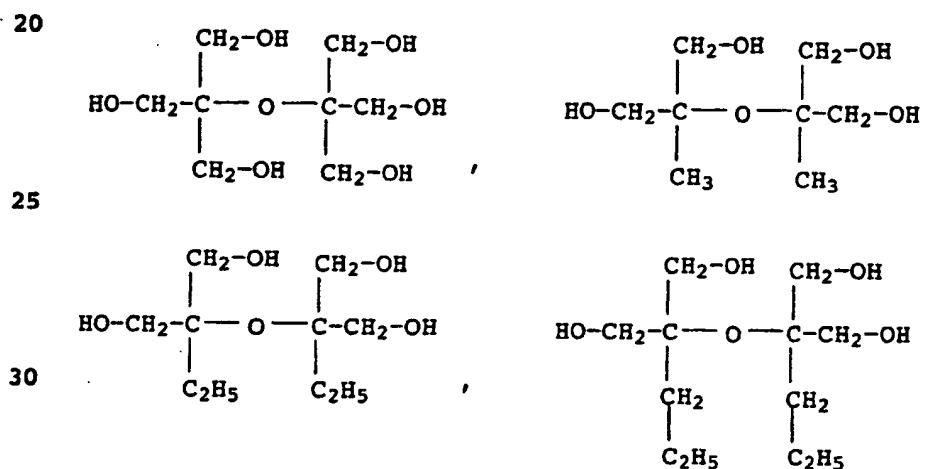
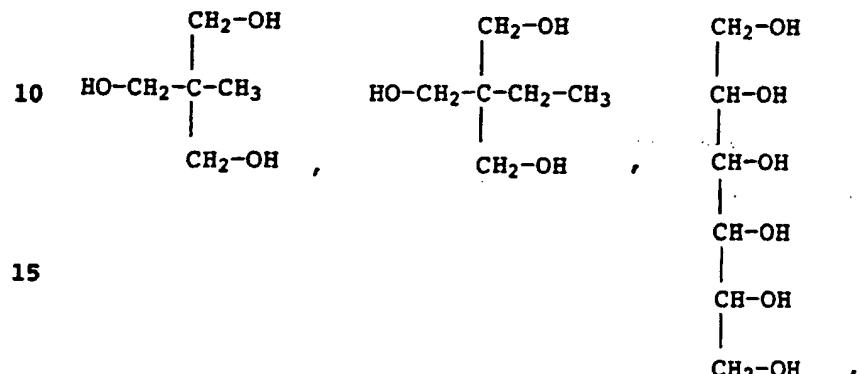
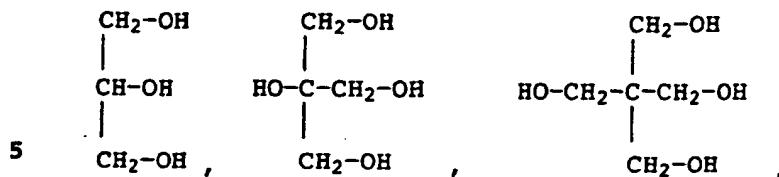
35 where m is from 2 to 8, preferably 2 to 6, but particularly preferably 2.

If n > 2, X is the radical of an n-hydric aliphatic or cycloaliphatic alcohol. These alcohols may be linear or branched, 40 and their carbon chains can be interrupted by one or more oxygen or sulfur atoms, by imino groups (-NH-) or C<sub>1</sub>-C<sub>4</sub>-alkylimino groups.

The group X is preferably derived from the following known 45 polyols:

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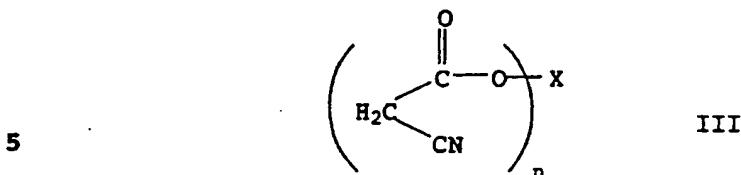


The 2-cyanoacrylic esters of the formula I where R<sup>1</sup> and R<sup>2</sup> are not linked via a nitrogen atom to the β-C atom are preferably obtainable by reacting cyanoacetic esters of the formula III

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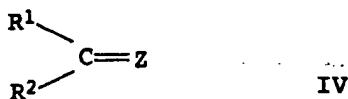
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with n mol of a compound (IV)

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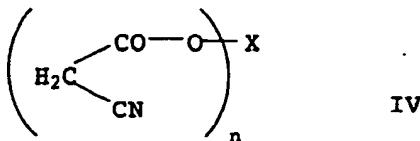


15 under the conditions of the Knoevenagel condensation. The reaction can, for example, be carried out in aromatic solvents such as toluene or xylene (see, for example, Organikum, 1976 edition, page 572). However, polar organic solvents such as dimethylformamide, dimethylacetamide, N-methylpyrrolidone, trialkyl orthoformate or alcohols such as n-propanol, n-butanol, ethylene glycol, diethylene glycol, ethylene glycol monomethyl ether, cyclohexanol or similar compounds are preferably used. If the starting compounds themselves form a liquid mixture, it is possible to dispense with an additional solvent. The reaction is preferably carried out at from 20 to 180°C, particularly preferably from 40 to 150°C. The pressure is preferably atmospheric pressure. The use of a catalyst or catalyst mixture may be advantageous depending on the reactivity of the compound IV employed. Examples of suitable catalysts are ammonium acetate, piperidine and  $\beta$ -alanine and 30 acetates thereof.

Catalysts which can additionally be used for the reaction if the reaction times are very long are Lewis acids such as  $\text{AlCl}_3$ ,  $\text{ZrCl}_4$ ,  $\text{TiCl}_4$  or, in particular,  $\text{ZnCl}_2$  in the amounts customary for this 35 purpose.

The 2-cyanoacrylic esters of the formula I where r is 1, ie. where one radical  $R^1$  or  $R^2$  is linked via a nitrogen atom to the  $\beta$ -C atom, can advantageously be prepared by reacting a cyano-40 acetic ester of the formula IV

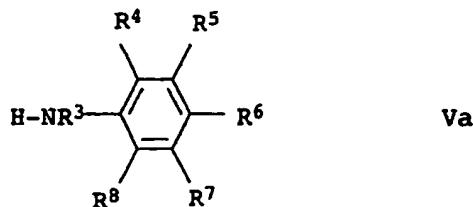
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with an aromatic amine of the formula Va

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in the presence of trialkyl orthoformate. Examples of trialkyl  
 10 orthoformates which have proven suitable are trimethyl orthoformate and triethyl orthoformate.

The cyanoacetic esters II can be prepared, for example, by reacting cyanoacetic acid or esters thereof with the appropriate  
 15 polyols  $X(OH)_n$  in the presence of a catalyst such as boric acid,  $Na_2CO_3$  or  $K_2CO_3$  or tetrabutyl orthotitanate, preferably in toluene or xylene.

The compounds according to the invention are outstandingly suitable for stabilizing organic materials against the action of  
 20 light, oxygen and heat.

Examples of plastics which can be stabilized by the compounds I according to the invention are:

25 polymers of mono- and diolefins, e.g. low and high density polyethylene, polypropylene, linear poly-1-butene, polyisoprene, polybutadiene, and copolymers of mono- or diolefins or mixtures of said polymers;

30 copolymers of mono- or diolefins with other vinyl monomers, e.g. ethylene/alkyl acrylate copolymers, ethylene/alkyl methacrylate copolymers, ethylene/vinyl acetate copolymers or ethylene/acrylic acid copolymers;

35 polystyrene and copolymers of styrene or  $\alpha$ -methylstyrene with dienes and/or acrylic derivatives, e.g. styrene/butadiene, styrene/acrylonitrile (SAN), styrene/ethyl methacrylate, styrene/butadiene/ethyl acrylate, styrene/acrylonitrile/methacrylate,  
 40 acrylonitrile/butadiene/styrene (ABS) or methyl methacrylate/butadiene/styrene (MBS);

halogenated polymers, e.g. polyvinyl chloride, polyvinyl fluoride, polyvinylidene fluoride and copolymers thereof;

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polymers derived from  $\alpha, \beta$  unsaturated acids and derivatives thereof, such as polyacrylates, polymethacrylates, polyacrylamides and polyacrylonitriles;

5 polymers derived from unsaturated alcohols and amines or their acrylic derivatives or acetals, eg. polyvinyl alcohol and polyvinyl acetate;

polyurethanes, polyamides, polyureas, polyphenylene ethers, poly-10 esters, polycarbonates, polyoxymethylenes, polysulfones, polyether sulfones and polyether ketones.

It is furthermore possible to use the compounds I according to the invention to stabilize surface coatings, eg. industrial coatings. Among these, particular attention is drawn to stoved coatings, and among these in turn to automotive coatings, preferably 15 two-layer coatings.

The compounds I according to the invention can be added in solid 20 or dissolved form to the coating material. Their good solubility in coating systems is a particular advantage in this context.

The compounds I according to the invention are preferably used for stabilizing polyolefins, especially polyethylene, poly-25 carbonates, polyamides, polyesters, polystyrene, ABS and polyurethanes. It is also possible, in particular, to stabilize sheets of said plastics.

For these applications, the compounds are employed in concentrations of from 0.01 to 5% of the weight of the plastic, preferably in a concentration of from 0.02 to 2% by weight. Combination with other stabilizers, for example antioxidants, metal deactivators or other light stabilizers, and with antistatic agents or flame retardants, is often advantageous. Examples of particularly 35 important costabilizers are sterically hindered phenols, and phosphites, phosphonites, amines and sulfur compounds.

Examples of suitable costabilizers are:

40 phenolic antioxidants such as

2,6-di-tert-butyl-4-methylphenol,

n-octadecyl  $\beta$ -(3,5-di-tert-butyl-4-hydroxyphenol)propionate [sic],

1,1,3-tris(2-methyl-4-hydroxy-5-tert-butylphenyl)butane,

45 1,3,5-trimethyl-2,4,6-tris(3,5-di-tert-butyl-4-hydroxybenzyl)-benzene,

1,3,5-tris(3,5-di-tert-butyl-4-hydroxybenzyl) isocyanurate,

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1,3,5-tris[ $\beta$ -(3,5-di-tert-butyl-4-hydroxyphenyl) propionylethyl] isocyanurate,  
 1,3,5-tris(2,6-dimethyl-3-hydroxy-4-tert-butylbenzyl) isocyanurate and pentaerythritol  
 5 tetrakis[ $\beta$ -(3,5-di-tert-butyl-4-hydroxy)propionate] [sic],

phosphorous-containing antioxidants such as tris(nonylphenyl) phosphite, distearyl pentaerythritol phosphite [sic], tris(2,4-di-tert-butylphenyl) phosphite,  
 10 tris(2-tert-butyl-4-methylphenyl) phosphite, bis(2,4-di-tert-butylphenyl) pentaerythritol diphosphite and tetrakis(2,4-di-tert-butylphenyl) 4,4'-biphenylene diphosphite,

sulfur-containing antioxidants such as  
 15 dilauryl thiodipropionate, dimyristyl thiodipropionate, distearyl thiodipropionate, pentaerythritol tetrakis( $\beta$ -laurylthiopropionate) and pentaerythritol tetrakis( $\beta$ -hexylthiopropionate),

20 sterically hindered amines such as bis(2,2,6,6-tetramethylpiperidyl) sebacate, bis(1,2,2,6,6-pentamethylpiperidyl) sebacate, bis(1,2,2,6,6-pentamethylpiperidyl) esters,  
 25 N,N'-bis(formyl)-bis(2,2,6,6-tetramethyl-4-piperidyl)-1,6-hexanediamine, the condensate of 1-hydroxy-2,2,6,6-tetramethyl-4-hydroxypiperidine and succinic acid,

30 the condensate of N,N'-(2,2,6,6-tetramethylpiperidyl)hexamethylenediamine and 4-tert-octylamino-2,6-dichloro-1,3,5-s-triazine, poly[3-(eicosyl/tetracosyl)-1-(2,2,6,6-tetramethyl-4-piperidinyl)-2,5-pyrrolidinedione],

35 tris(2,2,6,6-tetramethylpiperidyl) nitrilotriacetate, tetrakis(2,2,6,6-tetramethyl-4-piperidyl)-1,2,3,4-butanetetracarboxylic acid [sic], 1,1'-(1,2-ethanediyl)bis(3,3,5,5-tetramethylpiperazinone), the condensates of

40 4-amino-2,2,6,6-tetramethylpiperidines and tetramethylolacetylenediureas, and

2-(2'-hydroxyphenyl)benzotriazoles, 2-hydroxybenzophenones,  
 45 aryl esters of hydroxybenzoic acids,  $\alpha$ -cyanocinnamic acid derivatives,

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nickel compounds or  
oxanilides.

The compounds I according to the invention can be mixed, in  
5 particular with plastics, using all known apparatus and methods  
for mixing stabilizers or other additives into polymers.

The 2-cyanoacrylic esters I according to the invention are dis-  
tinguished by high compatibility with conventional types of  
10 plastic and by good solubility and excellent compatibility in  
conventional coating systems. As a rule, they have very little or  
no intrinsic color, are stable and nonvolatile at conventional  
plastic- and surface coating-processing temperatures and afford  
long-lasting protection to the materials treated with them. Above  
15 all, however, they show virtually no tendency to migrate in  
plastics.

UV radiation is divided into three regions: the UV-A region  
(320-400 nm), the UV-B region (290-320 nm) and the UV-C region  
20 (200-290 nm). The high-energy UV-C region is predominantly  
absorbed by the ozone layer. Radiation in the UV-B region is  
responsible in particular for the development of sunburn and skin  
cancer. UV-A radiation produces on lengthy exposure tanning of  
the skin but is also partly responsible for aging of the skin.

25 Because of the favorable solubility properties and the good  
absorption properties, especially in the UV-A region, the  
compounds according to the invention are particularly suitable  
for applications in cosmetics and dermatological products. The  
30 compounds can also be used advantageously for protecting cosmetic  
products such as perfumes, creams and lotions. Combinations with  
sunscreen agents which absorb in the UV-B region are particularly  
preferred. The 2-cyanoacrylic esters I are used for cosmetic  
formulations in concentrations of from 0.05 to 15%, preferably  
35 from 0.1 to 10%, of the total weight of the cosmetic formulation.

Other organic materials to which the compounds according to the  
invention can advantageously be added are pharmaceutical  
formulations such as pills and suppositories, photographic  
40 recording materials, especially photographic emulsions, and  
precursors for plastics and paints.

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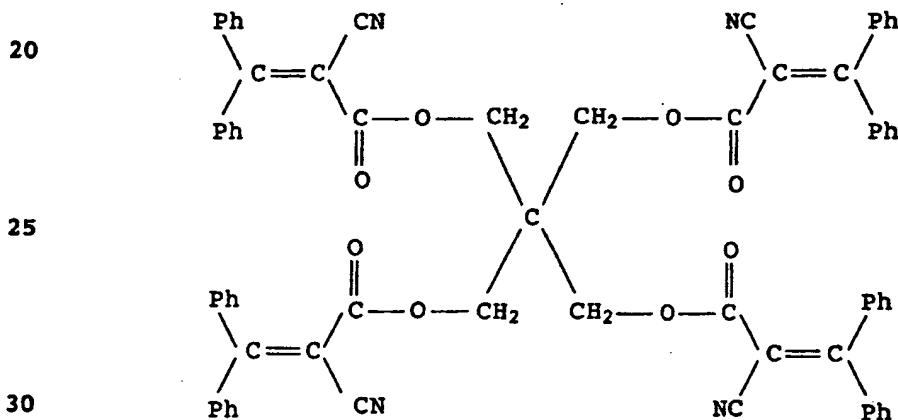
## Examples

## Preparation Examples

## 5 Example 1

16.2 g (0.04 mol) of 2,2-bis(hydroxymethyl)-1,3-propanediol tetracyanoacetate were dissolved in 100 ml of N,N-dimethylformamide (DMF) and heated to 80°C. To this were added dropwise under 10 a gentle stream of nitrogen 29.6 g (0.16 mol) of benzophenone imine (97% pure) dissolved in 25 ml of DMF, over the course of 2 h. The mixture was heated at about 100°C until ammonia evolution ceased. It was then cooled and 300 ml of ethanol were added. The product was initially oily and became solid after lengthy stirring. It was filtered off with suction and washed with ethanol.

37.5 g (88.4%) of theory of the compound of the formula



were obtained with melting point 123–126°C (glassy); UV (CH<sub>2</sub>Cl<sub>2</sub>):λ<sub>max</sub> = 310 nm, ε = 50,000.

## 35 Example 2

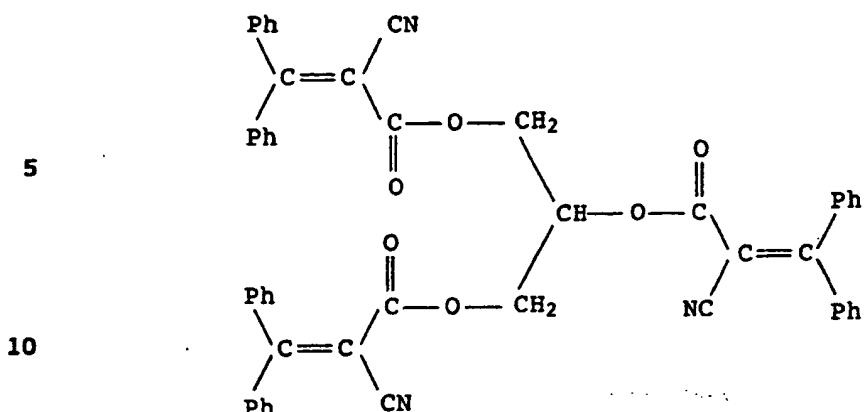
The compound of the formula

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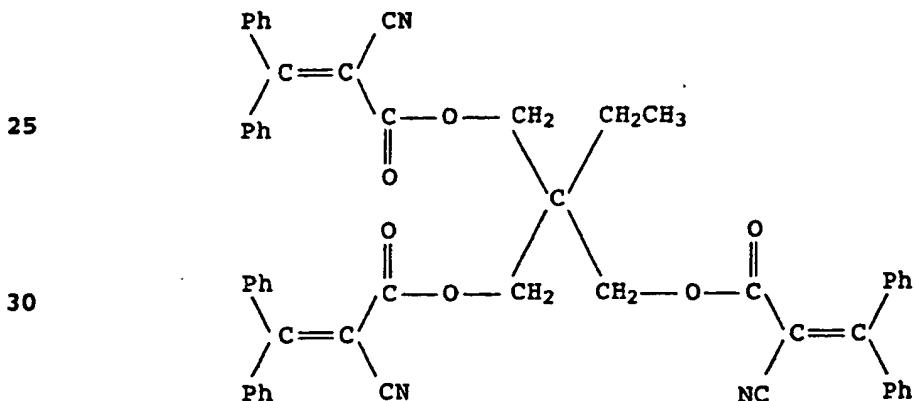
12



was prepared in a similar way to Example 1 from the appropriate  
 15 cyanoacetic ester and benzophenone imine; melting point:  
 100–104°C; UV (CH<sub>2</sub>Cl<sub>2</sub>):λ<sub>max</sub> = 310 nm, ε = 36,400.

## Example 3

20 The compound of the formula



35 was prepared in a similar way to Example 1 from the appropriate  
 cyano [sic] ester and benzophenone imine; melting point: 92°C;  
 UV (CH<sub>2</sub>Cl<sub>2</sub>):λ<sub>max</sub> = 308 nm, ε = 36,700.

## Example 4

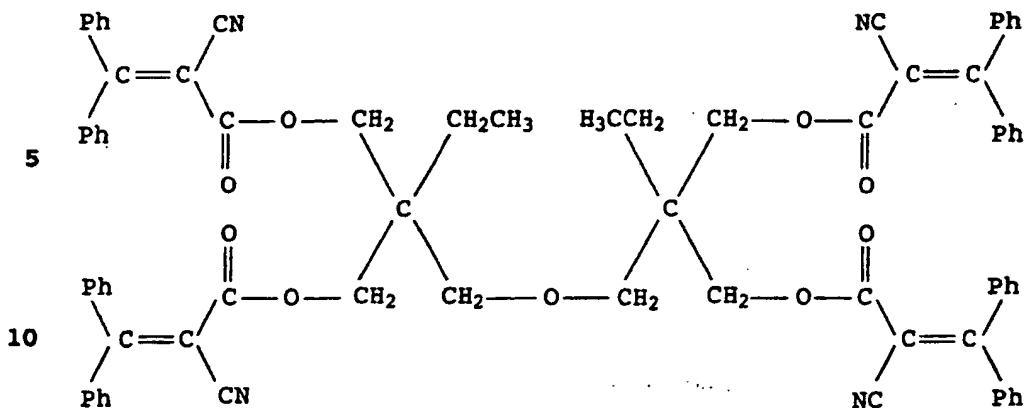
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The compound of the formula

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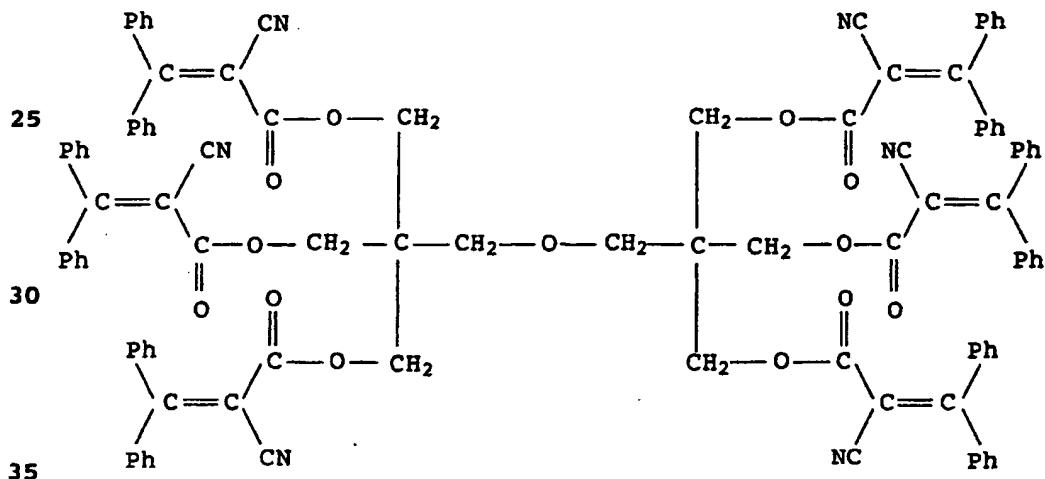
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was prepared in a similar way to Example 1 from the appropriate  
 15 cyanoacetic ester and benzophenone imine; melting point: 83–95°C;  
 UV ( $\text{CH}_2\text{Cl}_2$ ):  $\lambda_{\text{max}} = 308 \text{ nm}$ ,  $\epsilon = 51,700$ .

#### Example 5

##### 20 The compound of the formula



was prepared in a similar way to Example 1 from the appropriate  
 cyanoacetic ester and benzophenone imine; melting point 124–128°C;  
 UV ( $\text{CH}_2\text{Cl}_2$ ):  $\lambda_{\text{max}} = 308 \text{ nm}$ ,  $\epsilon = 76,000$ .

40

#### Example 6

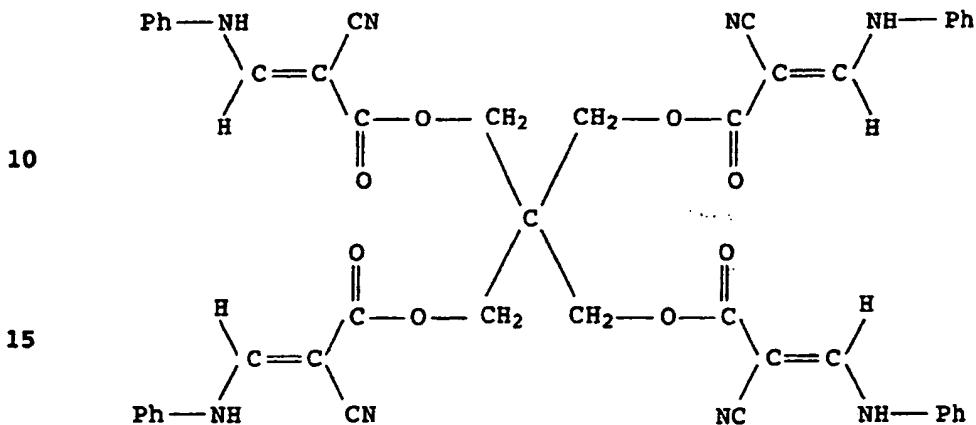
30.3 g (0.075 mol) of 2,2-bis(hydroxymethyl)-1,3-propanediol  
 tetracyanoacetate were refluxed with 29.8 g (0.32 mol) of aniline  
 45 and 52 g (0.35 mol) of trimethyl orthoformate for 6 h. Then 80 ml  
 of ethanol were added, and the suspension was refluxed for 1 h.

14

It was then filtered while hot under suction and the residue was thoroughly washed with ethanol.

55 g (90% of theory) of a yellowish compound of the formula

5

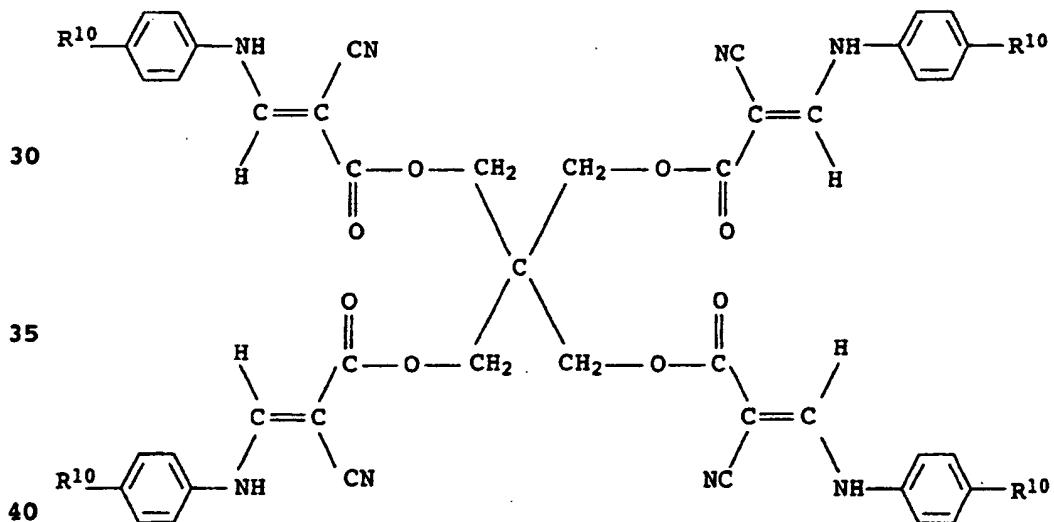


were obtained with melting point 298–300°C; UV (DMSO):  
 20  $\lambda_{\text{max}} = 322 \text{ nm}$ ,  $\epsilon = 98,000$  (DMSO = dimethyl sulfoxide).

Examples 7 and 8

The compound of the formula

25



$R^{10} = \text{CH}_3$  (Example 7) or  $\text{COOCH}_2\text{CH}_3$  (Example 8)

45 were [sic] prepared in a similar way to Example 6 from the appropriate cyanoacetic ester, the appropriate aromatic amine and trimethyl orthoformate; melting points: 321–323°C (Example 7) and

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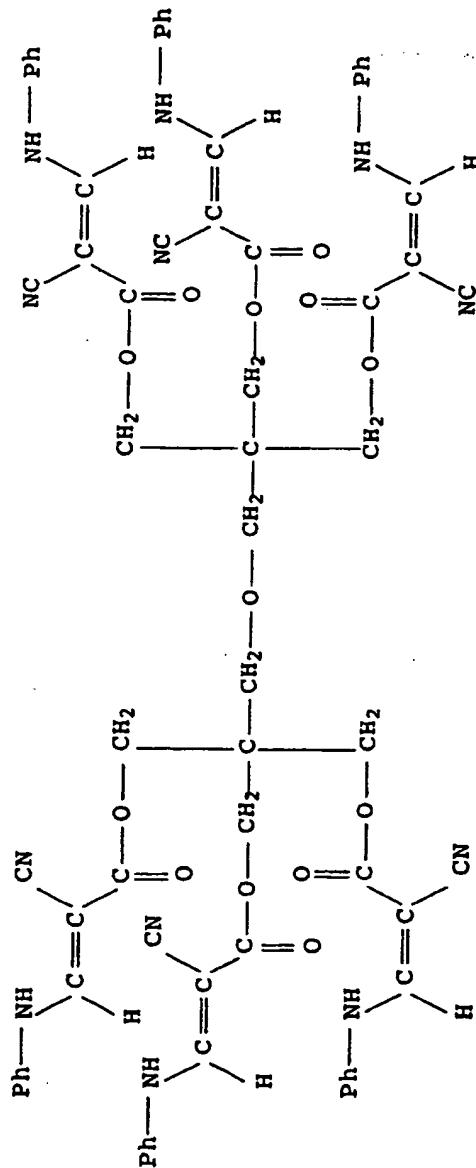
269–273°C (Example 8); UV (DMSO): $\lambda_{max}$  = 326 nm (Example 7) and 334 nm (Example 8),  $\epsilon$  = 99,000 (Example 7) and 150,000 (Example 8).

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### The compound of the formula



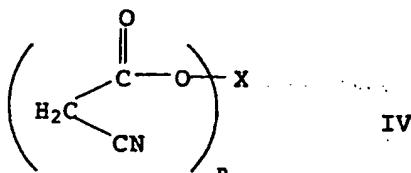
was prepared in a similar way to Example 6 from the appropriate cyanoacetic ester, aniline and trimethyl orthoformate; melting point 240–248°C; UV (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{\text{max}} = 320$  nm;  $\epsilon = 145,000$ .

## Examples 10-36

General preparation method for the reaction of cyanoacetic esters  
5 IV with aldehydes ( $R^1$  or  $R^2$  = hydrogen)

0.1 mol of an n-functional cyanoacetic ester IV,

10

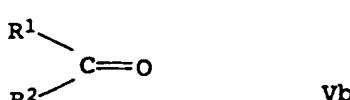


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which has been obtained by reacting cyanoacetic acid with the appropriate n-hydric alcohol in a conventional way,

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were [sic] reacted with 0.12 n mol of an aldehyde Vb



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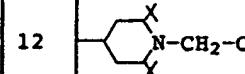
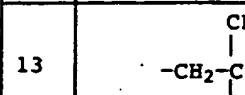
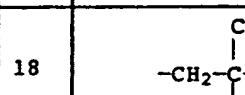
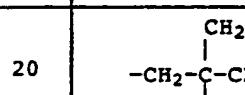
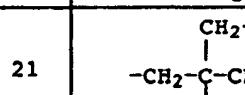
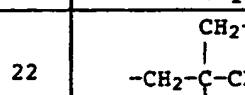
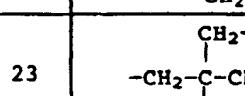
in 100 ml of N,N-dimethylacetamide [sic] in the presence of 0.5 ml of piperidine and 0.3 ml of glacial acetic acid. After 3 hours at 70°C, the precipitate was separated off, washed with methanol and water and dried.

30

Details of these experiments and the properties of the compounds I obtained are to be found in the following table.

35	No.	X	$R^1$ or $R^2$	$\lambda_{\text{max}}$ [nm]	Molar extinction coefficient $\epsilon$ [ $1 \cdot \text{cm}^{-1} \cdot \text{mol}^{-1}$ ]	Melting point [°C]	Yield [%]
40	10		$\text{H}_3\text{CO}-\text{C}_6\text{H}_4-$	342	57 000	>265	95
45	11		$\text{HO}-\text{C}_6\text{H}_3\text{X}-$	350	59 000	>265	70

## 2

NO.	X	R <sup>1</sup> or R <sup>2</sup>	* $\lambda_{\text{max}}$ [nm]	Molar extinction coefficient $\epsilon$ [l·cm <sup>-1</sup> ·mol <sup>-1</sup> ]	Melting point [°C]	Yield [%]
5						
12		H <sub>3</sub> CO 	336	47 000	>265	92
10	13		306	59 188	110-112	70
15	14		322	66 678	115-120	77
20	15		346	76 912	75-80	90
25	16		324	73 332	90-95	84
30	17		340	72 000	179-181	70
35	18		353	72 000	170-174	77
40	19		354	72 100	95-100	88
45	20		306	58 256	114-116	63
	21		322	67 090	95-102	74
	22		346	75 519	30-35	73
	23		322	57 601	168-170	67

No.	X	R <sup>1</sup> or R <sup>2</sup>	* λ <sub>max</sub> [nm]	Molar extinction coefficient ε [l·cm <sup>-1</sup> ·mol <sup>-1</sup> ]	Melting point [°C]	Yield [%]
5						
24	$\begin{array}{c} \text{CH}_2^- \\   \\ -\text{CH}_2-\text{C}-\text{CH}_2-\text{CH}_3 \\   \\ \text{CH}_2^- \end{array}$		338	68 000	103-105	74
10	$\begin{array}{c} \text{CH}_2^- \\   \\ -\text{CH}_2-\text{C}-\text{CH}_2-\text{CH}_3 \\   \\ \text{CH}_2^- \end{array}$		354	72 000	85-87	74
15	$\begin{array}{c} \text{CH}_2^- \\   \\ -\text{CH}_2-\text{C}-\text{CH}_2- \\   \\ \text{CH}_2^- \end{array}$		358	106 480	275-276	66
27	$\begin{array}{c} \text{CH}_2^- \\   \\ -\text{CH}_2-\text{C}-\text{CH}_2- \\   \\ \text{CH}_2^- \end{array}$		346	102 298	215-216	90
20	$\begin{array}{c} \text{CH}_2^- \\   \\ -\text{CH}_2-\text{C}-\text{CH}_2- \\   \\ \text{CH}_2^- \end{array}$		308	63 909	148-155	79
25	$\begin{array}{c} \text{CH}_2^- \\   \\ -\text{CH}_2-\text{C}-\text{CH}_2- \\   \\ \text{CH}_2^- \end{array}$		324	102 273	250	79
30	$\begin{array}{c} \text{CH}_2^- \\   \\ -\text{CH}_2-\text{C}-\text{CH}_2- \\   \\ \text{CH}_2^- \end{array}$		324	101 131	130-131	67
30	$\begin{array}{c} \text{CH}_2^- \\   \\ -\text{CH}_2-\text{C}-\text{CH}_2- \\   \\ \text{CH}_2^- \end{array}$		342	51 000	98-100	60
35	$\begin{array}{c} \text{CH}_2^- \\   \\ -\text{CH}_2-\text{C}-\text{CH}_2- \\   \\ \text{CH}_2^- \end{array}$		356	110 500	115-118	87
40	$\begin{array}{c} \text{CH}_2^- \quad \text{CH}_2^- \\   \quad   \\ -\text{CH}_2-\text{C}-\text{CH}_2-\text{O}-\text{CH}_2-\text{C}-\text{CH}_2- \\   \quad   \\ \text{CH}_2^- \quad \text{CH}_2^- \end{array}$		320	120 582	128-132	65
34	$\begin{array}{c} \text{CH}_2^- \quad \text{CH}_2^- \\   \quad   \\ -\text{CH}_2-\text{C}-\text{CH}_2-\text{O}-\text{CH}_2-\text{C}-\text{CH}_2- \\   \quad   \\ \text{CH}_2^- \quad \text{CH}_2^- \end{array}$		342	145 000	105-108	88

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No.	X	R <sup>1</sup> or R <sup>2</sup>	* $\lambda_{\text{max}}$ [nm]	Molar extinction coefficient $\epsilon$ [l·cm <sup>-1</sup> ·mol <sup>-1</sup> ]	Melting point [°C]	Yield [%]
5 35	$\begin{array}{c} \text{CH}_2- \\   \\ -\text{CH}_2-\text{C}-\text{CH}_2-\text{O}-\text{CH}_2-\text{C}-\text{CH}_2- \\   \qquad   \\ \text{CH}_2- \qquad \text{CH}_2- \end{array}$	$\text{H}_3\text{CO}-\text{C}_6\text{H}_3\text{X}_2-$	338	149 300	150-151	58
10 36	$\begin{array}{c} \text{CH}_2- \\   \\ -\text{CH}_2-\text{C}-\text{CH}_2-\text{O}-\text{CH}_2-\text{C}-\text{CH}_2- \\   \qquad   \\ \text{CH}_2- \qquad \text{CH}_2- \end{array}$	$\text{H}_3\text{CO}-\text{C}_6\text{H}_3\text{X}_2-$	352	145 000	135-140	51

\* UV measurements in  $\text{CH}_2\text{Cl}_2$ 

15 Example 37

Use Example: Migration test in polyethylene

0.3% by weight of the UV stabilizer indicated below was dissolved  
20 in polyethylene by extrusion twice at a polymer temperature of  
180°C, and then the polymer was granulated and blown to films  
100  $\mu\text{m}$  thick.

After storage at room temperature (20°C) or in an oven (50°C) for  
25 ten days, the surface of the film was assessed visually according  
to the following criteria:

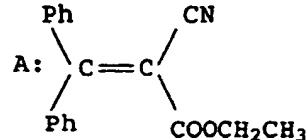
- + no deposit
- o slight deposit
- heavy deposit

30

The following table shows the UV stabilizers used and the results  
of the tests:

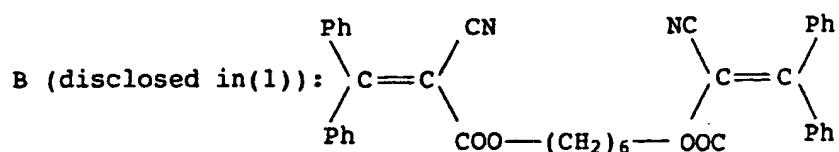
35	UV stabilizer	Storage at 20°C	Storage at 50°C
Compound from Example No. 1	+	+	
Compound A (for comparison)	o	-	
Compound B (for comparison)	-	-	

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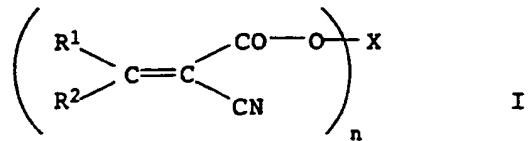
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We claim:

1. A 2-cyanoacrylic ester of the formula I

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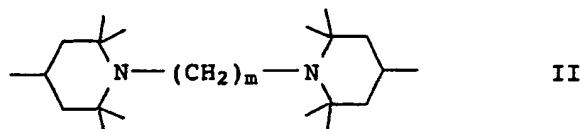
where  $R^1$  and  $R^2$  are each hydrogen or a radical having an iso- or heterocyclic ring system with at least one iso- or heteroaromatic nucleus, and at least one of the radicals  $R^1$  or  $R^2$  must be different from hydrogen,

20  $n$  is from 2 to 10, and

$X$  is, when  $n = 2$ , a radical of the formula II

25

25



where  $m$  is from 2 to 8, and

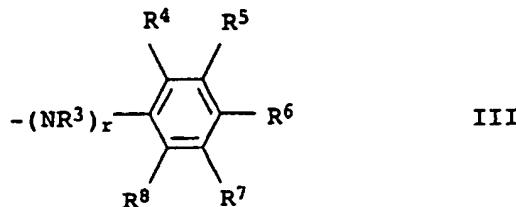
30  $X$  is, when  $n > 2$ , the radical of an  $n$ -hydric aliphatic or cycloaliphatic polyol having 3-20 carbon atoms, it also being possible for a cycloaliphatic radical to contain 1 or 2 hetero atoms, and for an aliphatic radical to be interrupted by up to 8 non-adjacent oxygen atoms, sulfur atoms, imino or  $C_1-C_4$ -alkylimino groups.

35

2. A 2-cyanoacrylic ester as claimed in claim 1, wherein one of the radicals  $R^1$  and  $R^2$  is a radical of the formula III

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where  $R^3$  is hydrogen or  $C_1$ - $C_{10}$ -alkyl,  $r$  is 0 or 1, and  $R^4$  to  $R^8$  are each, independently of one another, hydrogen,  $C_1$ - $C_8$ -alkyl, chlorine, bromine, cyano, nitro, amino, mono- $(C_1$ - $C_4$ -alkyl)amino, di( $C_1$ - $C_4$ -alkyl)amino, hydroxyl,  $C_1$ - $C_8$ -acyl,  $C_1$ - $C_8$ -acyloxy,  $C_1$ - $C_{18}$ -alkoxy,  $C_1$ - $C_{12}$ -alkoxy-carbonyl,  $C_3$ - $C_6$ -cycloalkyl or  $C_3$ - $C_6$ -cycloalkoxycarbonyl.

3. A 2-cyanoacrylic ester as claimed in claim 1 or 2, wherein  $R^3$  is hydrogen, methyl or ethyl.

10 4. A 2-cyanoacrylic ester as claimed in claims 1 and 2, wherein up to three of the radicals  $R^4$  to  $R^8$  are hydrogen,  $C_1$ - $C_4$ -alkyl, chlorine, cyano, hydroxyl, acetyl,  $C_1$ - $C_5$ -alkoxy,  $C_1$ - $C_8$ -alkoxycarbonyl or cyclohexoxycarbonyl, and the remainder 15 of these radicals are hydrogen.

5. A 2-cyanoacrylic ester as claimed in claims 1 to 4, wherein  $R^6$  is a hydroxyl group or a  $C_1$ - $C_4$ -alkoxy group.

20 6. A 2-cyanoacrylic ester as claimed in claims 1 to 5, wherein  $R^5$  and/or  $R^7$  are hydrogen, methyl or tert-butyl.

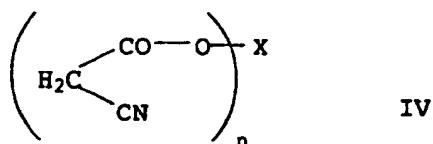
7. A 2-cyanoacrylic ester as claimed in claims 1 to 6, wherein  $r$  is 0.

25 8. A 2-cyanoacrylic ester as claimed in claims 1 to 7, wherein  $X$  is the radical of an  $n$ -hydric polyol having 3 to 12 carbon atoms, which may be interrupted in its linear or branched carbon skeleton by up to 3 non-adjacent oxygen atoms, and  $n$  30 is from 3 to 6.

9. A process for preparing 2-cyanoacrylic esters as claimed in claims 1 to 8, where  $r$  is 0, which comprises reacting a cyanoacetic ester of the formula IV

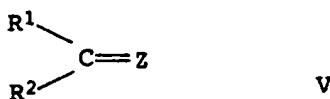
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with  $n$  mol of a compound of the formula V

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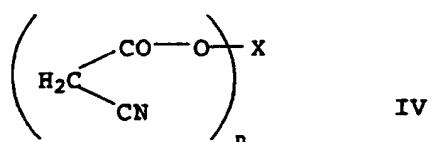
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where Z is oxygen or NH, under the conditions of the Knoevenagel condensation in a polar solvent and in the presence of a catalyst.

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10. A process for preparing 2-cyanoacrylic esters as claimed in claims 2 to 6 and 8, where r is 1, which comprises reacting a cyanoacetic ester of the formula IV

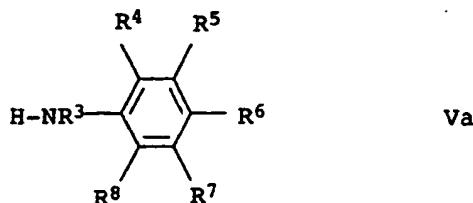
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with an aromatic amine of the formula Va

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in the presence of trialkyl orthoformate.

11. The use of the 2-cyanoacrylic esters as claimed in claims 1 to 8 as stabilizers, in particular against the action of light, for organic materials.

35

12. The use of the 2-cyanoacrylic esters as claimed in claims 1 to 8 as stabilizers, in particular against the action of light, in cosmetic or dermatological preparations.

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13. The use of the 2-cyanoacrylic esters as claimed in claims 1 to 8 as stabilizers, in particular against the action of light, in plastics or paints.

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14. Organic material stabilized against the action of light, oxygen and heat, which comprises from 0.01 to 10% by weight, based on the amount of organic material, of one or more 2-cyanoacrylic esters as claimed in claims 1 to 8.

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15. A cosmetic or dermatological preparation stabilized against the action of light, oxygen and heat, which comprises from 0.01 to 15% by weight, based on the amount of this preparation, of one or more 2-cyanoacrylic esters as claimed in claims 1 to 8.

10

16. A plastic or paint stabilized against the action of light, oxygen and heat, which comprises from 0.01 to 10% by weight, based on the amount of the plastic or paint, of one or more 2-cyanoacrylic esters as claimed in claims 1 to 8.

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